

## Utilization of Low NO<sub>x</sub> Coal Combustion By-Products

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### Introduction

The 1990 Clean Air Act Amendments established absolute caps on sulfur dioxide emissions and called for a two-million-ton reduction of emissions of nitrogen oxides (NO<sub>x</sub>) relative to 1980 levels. The compliance target dates include the year 1995 for Phase 1 and the year 2000 for Phase 2, depending on the boiler type and location (e.g. ozone nonattainment areas). Many coal-fired utilities have chosen retrofitting with low NO<sub>x</sub> burners as their strategy for meeting their share of the 1990 requirements. This increased use of low NO<sub>x</sub> burners however, has had a significant impact on the utilization of fly ash, a coal combustion by-product.

According to a NO<sub>x</sub> survey of the American Coal Ash Association (ACAA) in 1996, low NO<sub>x</sub> combustion has generated 5 to 11 million tons of fly ash. The total amount of fly ash generated from all coal-fired utilities was about 54 million tons. The survey also found that low NO<sub>x</sub> ash is not marketable because it has higher and more variable levels of unburned carbon than conventional ash. ACAA estimates that this low NO<sub>x</sub> ash costs utilities \$125 to \$275 million/year, ash marketers \$100 to \$200 million/year, and ash users \$125 to \$275 million/year [1]. This problem will be even more serious as the year 2000 is approaching for Phase 2 compliance.

At present, the biggest market for fly ash is as a replacement for cement in concrete applications. The pozzolanic properties of fly ash have made it a valuable material for this market. ASTM standard C618 has set a maximum limit of 6% LOI (primarily carbon) for fly ash in this application. In practice, a 3% LOI limit is commonly recognized by the market.

It is difficult to reduce the carbon content of fly ash generated in a low NO<sub>x</sub> combustion unit because low NO<sub>x</sub> combustion requires low oxygen and/or low temperature combustion conditions. It is generally recognized that the lower the NO<sub>x</sub> emissions, the higher the unburned carbon content of the generated ash. In order to meet NO<sub>x</sub> emission requirements, power plants using low NO<sub>x</sub> burners typically experience an increase of 3 to 6% in the unburned carbon content in their fly ash [2-5].

There is also a need to expand fly ash utilization. Based on a 1995 ACAA survey, only 25% of the 54 million tons of ash generated annually are currently being utilized. This disposal of more than 30 million tons of fly ash represents a serious environmental problem; indeed, many utilities are currently facing difficulties with ash disposal. Increased ash utilization will not only solve this disposal problem, but also bring about other environmental benefits. For example, when a ton of ash is used to replace the cement in concrete, 0.8 ton of CO<sub>2</sub> emissions can be reduced from the production of cement. At present, ash utilization is generally limited within a 150 miles radius of its generation location. Transportation cost is the major issue. To expand ash utilization, it is necessary to increase the value of fly ash to allow it to be transported a greater distance.

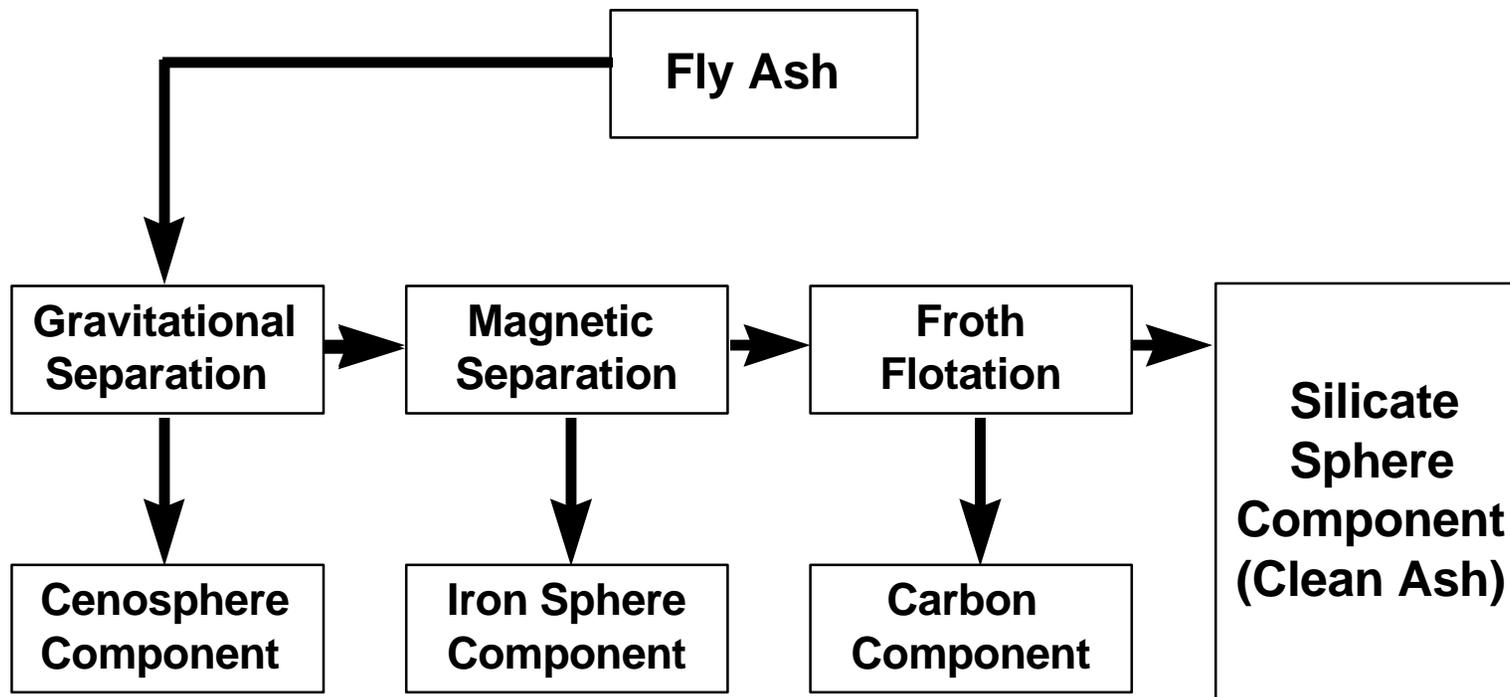
## **Objectives**

There were two major objectives for this study. The first objective was to develop a separation process to yield high quality fly ash materials. The second objective was to develop utilization technologies so that new applications and markets for fly ash can be generated.

## **Separation Technologies**

For a material to have reasonable commercial value, this material must be well defined and be able to meet industrial specifications. It must also be available at consistent quality levels and in sufficient quantities to meet market demands. Characterization of fly ash obtained from various sources shows that the mineral components of the ashes are similar, even though the bulk chemistry of these ashes may vary widely. Based on scanning electron microscope studies, the major mineral components in fly ash can be categorized into silicates, iron oxides, low density silicates (cenospheres) and unburned carbons. The silicates are usually present as spherical particles. They are believed to be the melted products of clays, feldspars, quartz, calcite, and other common minerals in coal. The iron oxides are usually spherical magnetite. They are believed to be derived from pyrite, hematite, siderite, and limonite in the coal. Low density silicates are frequently high alkaline silicates which entrapped gas to yield hollow spherical particles. The lower melting point of these high alkaline silicates may facilitate gas entrapment. Unburned carbons are generally chars with irregular shapes and wide range of particle sizes. Variations in fly ash bulk chemistry are usually due to the changes of ratios of these mineral components.

Based on these characterization results, a separation process has been designed and tested. A schematic flow sheet of the separation process is shown in Figure 1. This process consists of a gravitational separation process to separate the cenospheres, a magnetic separation process to separate the iron oxide spheres, and a froth flotation process to separate the unburned carbon [6, 7]. The material left after these separations is designated as clean ash. Depending on user needs, individual process separation circuits can be switched in sequence, eliminated, or new circuits can be added. This offers great flexibility for meeting varying requirements due to changes in ash (e.g. from a fuel switch in a power plant) and markets. For example, a froth flotation circuit may be all that is needed for ash processing if the material is to be used only for cement replacement. But magnetic separation would have to be included if the cleaned ash is to be used for refractory applications. For plastic filler applications, a hydrocyclone circuit would need to be included in order to separate out the appropriate fine particle fraction.



**Figure 1. Fly Ash Separation Process**

Table 1 shows the results of separation for an AEP low NO<sub>x</sub> fly ash sample. Fly ash was mixed with water at 20% solids content in a pilot plant operation running at 200 lb/hr. The slurry was fed into a tank where the cenospheres were skimmed off from the top since these cenospheres have a density less than that of water. Then the slurry was fed into a magnetic drum separator to recover the magnetic spheres. After magnetic separation, the slurry was conditioned with an oil collector at a dosage of 2 lb/ton. The oil has an affinity for carbon and is preferentially adsorbed onto the carbon particles. The slurry was then fed into a flotation machine where air was bubbled through it. During flotation, the rising air bubbles collided with the oil coated carbon particles and attached themselves to these particles due to a hydrophobic interaction. This caused the carbon particles to float to the top of the flotation cell, where they were skimmed off. This flotation operation left the clean ash in the cell. This clean ash was then filtered and dried. The carbon fraction was transferred to another flotation cell and re-floated to upgrade the carbon content in the carbon concentrate. The reject from the carbon-refloat operation was then returned to the first flotation cell. A typical operation showed the carbon (LOI) content in the clean ash to be only 0.40%, greatly reduced from the 21.70% carbon content of the as-received fly ash. The carbon concentrate had a carbon content of 67.70%. The magnetic concentrate contained 77.18% iron oxide.

<b>Table 1. Separation Products From An AEP Low NOx Sample</b>					
	<b>As-Rec'd.</b>	<b>Clean Ash</b>	<b>Carbon</b>	<b>Cenosphere</b>	<b>Magnetics</b>
SiO <sub>2</sub>	44.00	58.6	19.26	57.58	14.34
Al <sub>2</sub> O <sub>3</sub>	22.4	29.2	9.92	29.57	8.2
Fe <sub>2</sub> O <sub>3</sub>	5.3	5.2	0.04	3.71	77.18
MgO	0.86	1.11	0.5	1.38	0.5
CaO	0.76	0.85	0.5	0.35	0.45
Na <sub>2</sub> O	0.32	0.42	0.05	0.38	0.04
K <sub>2</sub> O	2.35	3.16	0.8	4.23	0.43
TiO <sub>2</sub>	1.11	1.33	0.7	0.91	0.31
P <sub>2</sub> O <sub>5</sub>	0.03	0.09	0.22	0.03	0.01
MnO	0.01	0.02	0.01	0.02	0.06
LOI	21.7	0.40	67.7	2.4	-1.4
Total	98.84	100.38	99.89	100.83	100.28

This process has been applied to many different fly ash samples obtained from various power companies including Detroit Edison, Consumers Power, Baltimore Gas and Electric, Virginia Power, American Electric Power, Nevada Power. Table 2 shows typical results obtained on these ashes. Note that clean ash with less than 1% carbon content can always be obtained.

<b>Table 2. Carbon Removal by Froth Flotation</b>				
<b>Ash Type</b>	<b>F (#1)</b>	<b>F (#2)</b>	<b>F+C</b>	<b>C</b>
LOI, As-Received	21.70	7.25	4.35	4.00
LOI, Clean Ash	0.40	0.61	0.90	0.96

## **Utilization Technologies**

Five generic areas have been identified as potential markets for utilization of separated, quality-controlled fly ash products. They are i) cement and concrete, ii) ceramics and refractories, iii) plastic fillers, iv) metal matrix composites, and v) carbon adsorbents. Each area has the potential to consume a large volume of fly ash. Some are also high-value-added applications, such as ceramics and carbons. Currently, the domestic consumption of cement is about 76 million tons per year. It is estimated that 20% of this cement can be replaced with fly ash. Ceramic and refractory products have a market volume of about 40 million tons per year. Possibly more than 2 million tons of fly ash can enter into this market. The fillers market is about 17 million tons a year (including 8 million tons in plastics and 9 million tons in non-plastics). It is estimated that 2 million tons can be replaced by fly ash. The carbon market may include 500,000 tons of activated carbon and several million tons of carbon black. These represent major target markets for the carbon product separated from fly ash, if this carbon product is not utilized as a fuel. Cenospheres are a good insulator and work very effectively as lightweight fillers (specific gravity about 0.64). This material has been traditionally harvested from ash ponds as “floaters.” They have a number of well-established markets, including lightweight plastics, insulating panels, golf balls, autobody fillers, and PVC floor coverings. Their utilization is not revisited in this study. Iron oxide spheres can be utilized as a heavy media commonly utilized in coal cleaning. No new technology is necessary for this application.

### **A. Cement and Concrete Applications**

Cement and concrete is currently the largest user of fly ash. It is known that up to 50% of the cement in concrete can be replaced by fly ash without compromising concrete performance. This is due to the pozzolanic and/or cementitious properties of the ash. Replacing cement with fly ash provides a significant cost savings for concrete applications. In addition, the use of fly ash in concrete offers benefits such as improved workability, lower water requirements, less heat hydration, improved resistance to alkali aggregates and sulfur attack, and permeability reduction. Cement and concrete users are well aware of these advantages and have been looking for--and purchasing--appropriate fly ash.

The critical specifications which most fly ash materials fail to meet is the Loss on Ignition (LOI) or carbon content requirement. One of the major properties of concrete is its air content. It is necessary to develop and hold entrained air in concrete to increase its freeze-thaw resistance. To achieve this property, an air entraining agent is typically added. Fly ashes containing high carbon contents typically require large dosages of this air entraining agent since unburned carbon adsorbs the agent, reducing its effectiveness. Even with large dosages of air entraining agent, the air content and slump of the concrete are still difficult to control. Fly ash carbon also increases the required water-to-cement ratio of the concrete, so that the variations in carbon content also make it very difficult to properly control this ratio. High carbon content in the fly ash will also stain or darken concrete.

One concern which has been raised about the use of clean ash in cement and concrete applications is whether or not the clean ash will lose its pozzolanic properties after being processed in water. Experiments to address this issue have been conducted in cooperation with Detroit Edison, Consumers Power, and Holnam Cement. This work has shown that clean ash can be used successfully in cement and concrete applications. [8]. The tests were conducted following a standard procedure for concrete Grade 35S, one of the most commonly used concrete mixes in Michigan. Grade 35S concrete is designated by the Michigan Department of Transportation (MDOT) as having a moderate design compressive strength of 3,500 psi at 28 days [9]. Slump at  $3 \pm 1$  inch and entrained air at  $7 \pm 1\%$  represent common practice for general construction. Table 3 shows test results obtained using a Class F low  $\text{NO}_x$  ash. The as-received ash had a 7.25% LOI while the clean ash had a 0.61% LOI. The data includes the actual mix proportions for the concrete mixes, as well as the slump, air content, and density for the fresh concrete. Observed 7, 28, and 91 days compressive strengths are also shown. Concrete without any cement replaced by fly ash (Mix 1) was used as a control mix for comparison. Note that fly ash was used to replace 20% of the cement in the mixture.

The water demand for the control was 296.5 pounds per cubic yard in order to achieve the desired slump ( $3 \pm 1$  inch), The clean ash mix required only 278 pounds water per cubic yard to achieve this same slump. This demonstrates that the clean ash improves the workability of concrete, primarily due to the spherical shape and improved fluidity of the fly ash particles. As-received ash contains unburned carbon, which is angular and absorbs water. Accordingly, the concrete produced using uncleaned ash required more water than that made using the cleaned ash.

The design goal for air content was  $7 \pm 1\%$ . Both the control and the clean ash mix had no problem reaching this goal at about 10 ounces per cubic yard dosage of air entraining agent (AEA). However, concrete produced using as-received, uncleaned ash could never reach this goal even with increased air entraining agent dosage. Mix #1 used about the same dosage as the clean ash, but could only obtain an air content of 2.2%. Increasing the air entraining agent by 40% (Mix #2) and 50% (Mix #3) did not improve the air content. Because of this failure, the as-received ash would be excluded from 35S concrete applications.

All of the concretes tested met the 3,500 psi requirement at 28 days. The clean ash mix exhibited higher strength (5,447 psi) than the control (5,006 psi) at 91 days. This proves that the pozzolanic properties are still maintained by the clean ash. The as-received ash mixes generally showed highest strength, possibly due to their very low air content.

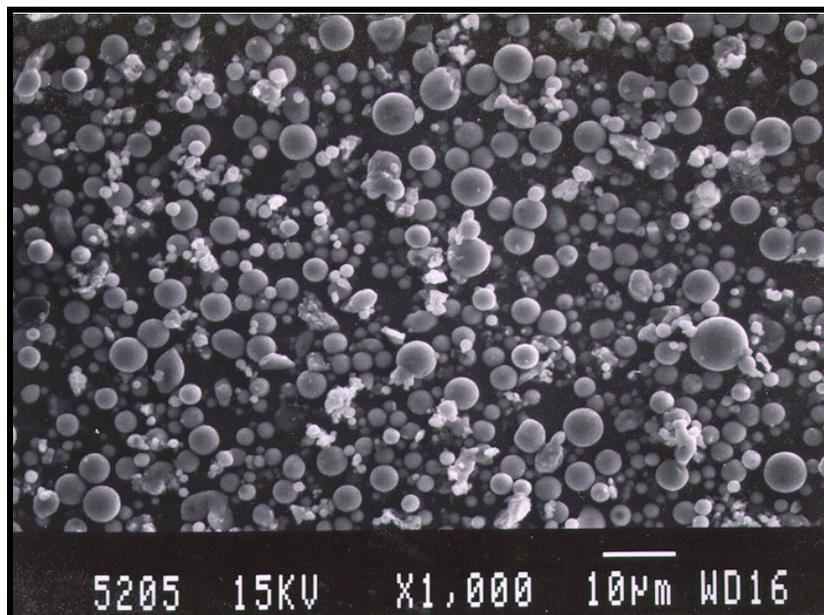
**Table 3. Properties of 35S Concrete With 20% of the Cement Replaced  
by As-Received and Cleaned Class F Ash**

<b>Samples</b>	<b>0% Mix 1 (Control)</b>	<b>As-rec. Ash, #1</b>	<b>As-rec. Ash, #2</b>	<b>As-rec. Ash, #3</b>	<b>Clean Ash</b>
W/C ratio	0.50	0.475	0.465	0.460	0.445
Cement, lb/cu <sup>3</sup>	564	451	451	451	451
Fly ash, lb/cu <sup>3</sup>	0	141	141	141	141
Water, lb/cu <sup>3</sup>	296.5	295.6	289.7	286.7	278.0
Fine Agg.	1150	1076	1093	1100	1125
Coarse Agg.	1845	1845	1845	1845	1845
AEA, oz/cu <sup>3</sup>	9.9	10.9	14.4	15.5	10.9
Slump, in	3.6	2.5	3.0	3.0	3.0
Air, (%)	7.8	2.2	2.5	2.4	7.0
Density, lb/ft	145.4	150.8	152.2	152.0	145.2
7 day strength (psi)	3534 3601 3516	3629 3421 3625	4046 4011 4011	3851 4081 3852	2827 2986 3145
Average	3550	3558	4022	3928	2986
28 day strength (psi)	4686 4597 4654	5007 4912 4781	5159 5406 5370	5477 5247 5636	4700 4682 4400
Average	4646	4900	5312	5506	4594
91 day strength (psi)	5088 4947 4982	6042 5548 5830	6890 6996 7120	6749 6855 6519	5247 5548 5548
Average	5006	5807	7002	6708	5447

## B. Plastic Filler Applications

Mineral fillers are widely used in plastic products to improve performance and reduce resin costs. More than 17% of plastic products contain mineral fillers. Fly ash, since it is essentially a spherical aluminosilicate powder, represents a potentially attractive replacement for these mineral fillers. It may offer cost, processing, and perhaps even property advantages over traditional fillers.

Calcium carbonate, the most common mineral filler, accounts for about 70% of the current plastic filler market. To determine if clean fly ash can substitute for calcium carbonate, various tests have been conducted [10]. A commercial  $\text{CaCO}_3$  filler (Gama-Sperse CS-11) commonly used in polymers was acquired from Georgia Marble Company. This filler has a mean particle size of 3 microns and has been precoated with 1% stearate by the manufacturer to improve its affinity with polymers. Clean ash obtained from an AEP low  $\text{NO}_x$  ash was evaluated as a replacement for this commercial filler. Since this ash had a mean particle size of 30 microns, a cyclone was employed to separate out the fine fraction of the clean ash. This fine fraction of the clean ash had a mean particle size of 4.1 microns. A Dow Corning Z-6032 silane coupling agent was selected to coat the fine clean ash to provide increased surface affinity for the polymers. Figure 2 shows an SEM photograph of the fine clean ash. Polypropylene (PP), low density polyethylene (LDPE), and high density polyethylene (HDPE), manufactured by Fina Oil, Exxon, and Phillips Petroleum, respectively, were investigated. The polymers were first compounded (mixed) with the fillers at filler contents of 0, 10, 20, 40 and 80 parts per hundred parts of resin (phr). The compounding was conducted in a Brabender Plasti-Corder torque-rheometer at 50 rpm for 30 minutes. The mixing temperatures were 250°, 190°C and 200°C for PP, LDPE, and HDPR, respectively.



**Figure 2. Particle Shape of Fine, Clean AEP Ash.**

After compounding, the materials were tested with an Arburg 221-75-350 injection molding machine to determine if the compounded plastic-filler mixes could be injection molded. Injection moldability is inversely proportional to material viscosity. The addition of a filler to a polymer increases the viscosity of the mix during injection molding, thus decreasing its moldability. If the filler content exceeds a certain level, the compound may become so viscous that it cannot be injection molded successfully. Mechanical testing specimens were produced from the polymer mixes could be injection molded successfully. These specimens were then tested in tension to determine the modulus of elasticity, elongation, yield and ultimate strength of each material. This testing was done in accordance with ASTM standard D-638 using an Instron testing system. Since all four materials exhibited similar behavior, only the LDPE results will be described in detail. Results obtained on other materials can be found in an earlier publication [10].

Table 4 presents the injection molding test results. The LDPE containing 80 phr CaCO<sub>3</sub> filler could not be injection molded successfully even under maximum temperature (250°C Zone II temperature) and pressure (2200 psi) conditions. For comparison, LDPE containing 80 phr fine clean ash filler could be injection molded successfully at 230°C and 900 psi pressure. This demonstrates that polymers containing fine clean ash exhibit better injection moldability than those filled with traditional calcium carbonate fillers.

<b>Table 4. Injection Molding Test of Low Density Polyethylene With Fillers</b>									
Fillers	Filler Content phr	Zone I Temp. °C	Zone II Temp. °C	Zone III Temp. °C	Zone IV Temp. °C	Injection Velocity Dial*	Injection Pressure psi	Holding Pressure psi	Mold Temp. °F
None	0	210	220	210	200	5.0	500	100	100
Fly Ash CaCO <sub>3</sub>	10	210	220	210	200	5.0	500	100	100
	10	210	220	210	200	5.0	500	100	100
Fly Ash CaCO <sub>3</sub>	20	220	230	220	210	5.0	700	100	100
	20	220	230	220	210	5.0	700	100	100
Fly Ash CaCO <sub>3</sub>	40	220	230	220	210	5.0	700	100	100
	40	220	230	220	210	5.0	900	100	100
Fly Ash CaCO <sub>3</sub> *	80	220	230	220	210	5.0	900	150	100
	80	240	250	240	230	5.0	2200	150	120
* This material couldn't be injected even at the maximum pressure of 2200 psi.									

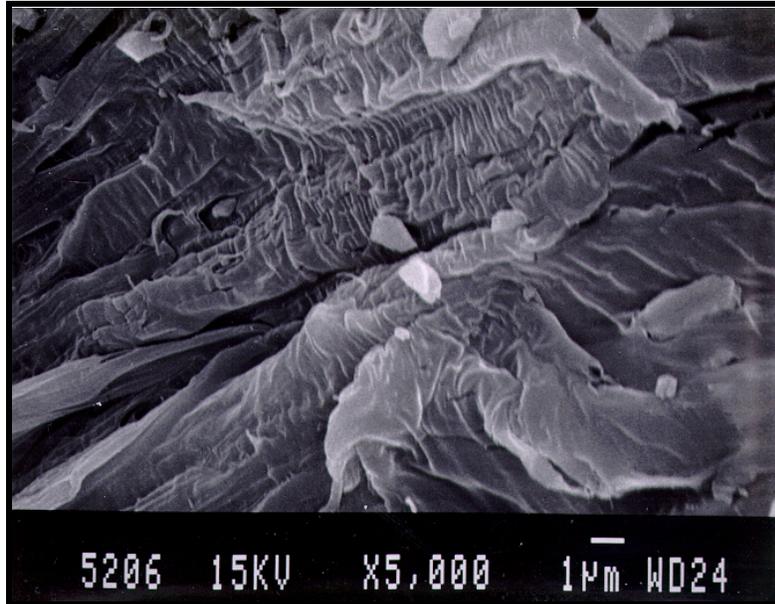
Ultimate tensile strength, yield strength, elongation and Young's modulus are the most important mechanical properties for polymer materials. Filler content, particle size, particle size distribution, shape, mixing quality, and bonding characteristics all affect these mechanical properties. As a rule, higher filler content leads to higher yield strength and increased Young's modulus. This is generally accompanied by a decrease in elongation, since the filler particles restrict deformation of the polymer. Fillers affect the ultimate tensile strength (UTS) of the polymer in two ways. First, they generate stress concentrations and initiate cracks, lowering the UTS. Second, if the particles have the proper

shape and exhibit a strong bonding with the polymer matrix, they may serve to reinforce polymer, resulting in a higher UTS. The presence of large filler particles tends to reduce both the UTS and elongation of the material. Table 5 lists the mechanical properties of LDPE filled with both clean fine ash and calcium carbonate fillers. As anticipated, the yield strength and Young's modulus of the materials increase, and UTS and elongation decrease, as the filler content increases. Clean fly ash outperforms calcium carbonate in every category evaluated. At 40 phr, the fine clean ash filler is better than calcium carbonate filler in ultimate tensile strength by 28% (2449 psi vs 1905 psi), in yield strength by 28% (738 psi vs 574 psi), in elongation by 2% (450 vs 442), and in Young's modulus by 41% (47.3 ksi vs 33.6 ksi).

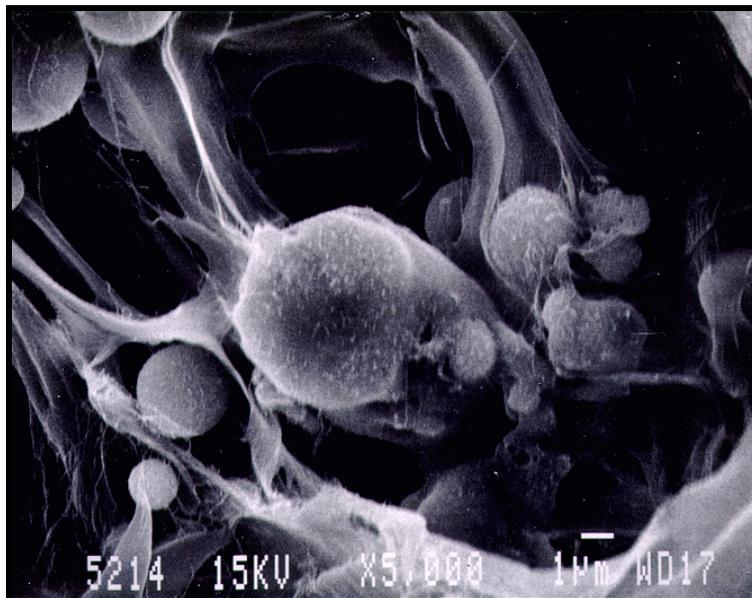
<b>Fillers</b>	<b>Filler Content (phr)</b>	<b>Ultimate Tensile Strength (psi)</b>	<b>Yield Strength (psi)</b>	<b>Elongation (%)</b>	<b>Young's Modulus (ksi)</b>
None	0	3336	485	467	27.5
Fine, Clean Ash CaCO <sub>3</sub>	10	3463	557	467	36.0
	10	3255	545	467	33.4
Fine, Clean Ash CaCO <sub>3</sub>	20	2635	560	462	39.4
	20	2563	573	483	33.6
Fine, Clean Ash CaCO <sub>3</sub>	40	2449	738	450	47.3
	40	1905	574	442	33.6
Fine, Clean Ash CaCO <sub>3</sub>	80	2377	888	46.6	90.5
	80	—	—	—	—

The superior performance of fine clean ash over conventional calcium carbonate fillers can be explained in terms of its ability to form a strong bond with the polymer matrix. Figure 3 shows an SEM image of the fracture surface of HDPE containing a calcium carbonate filler. Calcium carbonate particles appear to exhibit little bonding with the polymer matrix. On the other hand, fine clean ash particles exhibit very good bonding with PP, as shown in Figure 4.

To evaluate if fine clean ash filler is suitable for commercial applications, a large amount of LDPE/fine clean ash compound was prepared and shipped to U.P. Plastics for testing. This material was used to produce two commercial automotive components--a Chrysler trim clip and a GM wiring harness support. The Chrysler trim clip was chosen because of its symmetric cavity layout and because the major surfaces of the clip were parallel to each other and perpendicular to the runner. The GM wiring harness support contained large radii and smooth surfaces which would provide a good indication of the surface quality that could be expected from compounds containing fine clean ash.

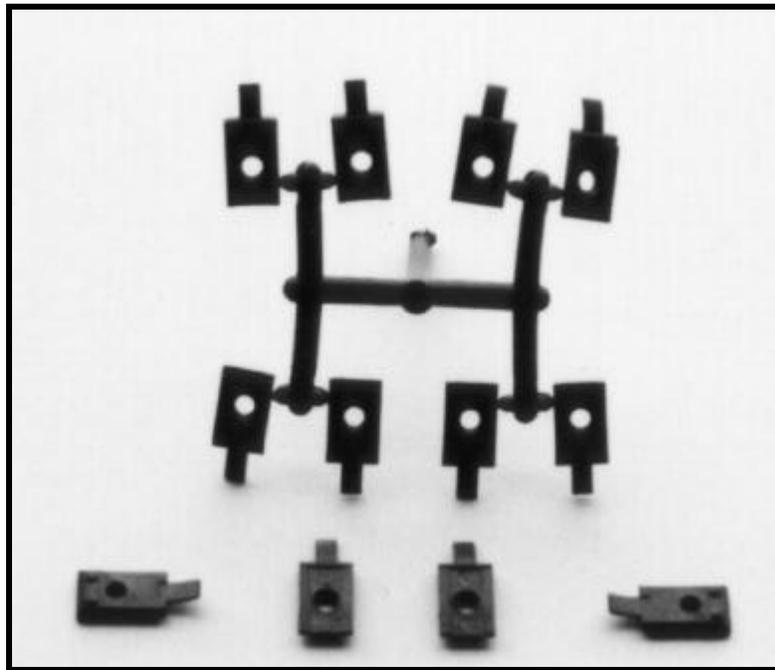


**Figure 3. Fracture Surface of HDPE with 40 phr CaCO<sub>3</sub> Filler.**



**Figure 4. Fracture Surface of Polypropylene with 40 phr Fine, Clean AEP Ash.**

The molding tests were conducted with a VanDorn Model 75-RS-4F injection molding machine. The Chrysler trim clip was molded first due to its smaller size. This test went very smoothly. Material flowed well, cavities were filled uniformly, lines were well defined and clips could be stripped from the mold without the use of a mold release agent. Figure 5 shows some of the parts produced during this trial. Molding of the GM wiring harness support proceeded very well. The ash-filled LDPE met all molding requirements and the surface finish obtained on the surfaces of the part was very smooth. Figure 6 shows a photograph of the GM wiring harness support produced under the program.



**Figure 5. Chrysler Trim Clips Produced from a LDPE/Fine, Clean Ash Compound**

### **C. Refractory Applications**

Un-processed fly ash has a chemical composition similar to that of an impure clay. Accordingly, fly ash has good potential for replacing a portion of the clay contained in many ceramic products. The residual carbon, cenospheres and magnetic particles present in unprocessed ash, however, have detrimental effects on the processing characteristics and quality of most ceramic products, including firing temperature, color, mechanical properties and physical properties. The use of beneficiated fly ash, however, can overcome these limitations. Indeed, clean ash free of residual carbon, cenospheres and magnetic particles may be even more suitable than naturally-occurring clays for production of technological ceramics such as mullite. Mullite is a commonly-used industrial refractory exhibiting good chemical stability, high heat resistance, low thermal expansion, good strength and reasonable toughness. It has been used in metallurgical furnaces, turbine engine parts, protective coatings, electronic substrates, infrared transmitting windows and ceramic composites. The major raw material

for synthesizing mullite is alumina, which is priced at about \$1,000 per ton. Fly ash contains approximately 30% alumina. Accordingly, combining equal amounts of fly ash and alumina can produce the target mullite composition. This approach requires substantially less alumina than conventional mullite fabrication methods, resulting in considerable cost savings for mullite producers. Research is needed, however, to develop a method of synthesizing fly ash mullite which meets commercial standards.



**Figure 6. GM Wiring Harness Support Produced from a LDPE/Fine, Clean Ash Compound.**

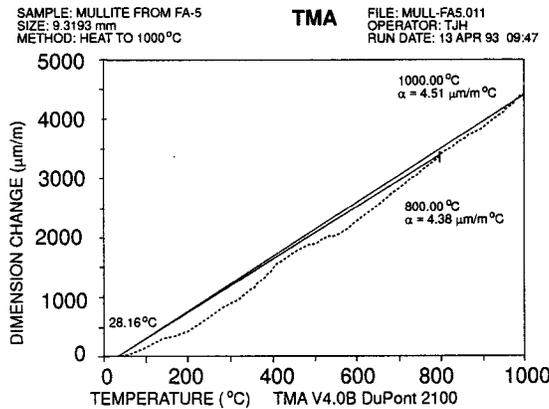
Commercial mullite is generally produced by fusion in an electric arc furnace. Other ways of producing the material include reaction sintering, chemical vapor deposition, and sol-gel processing. Reaction sintering of fly ash-alumina mixtures was chosen for this project primarily because it is a relatively low cost process ideally suited for making refractory products from fine powders. A Class F clean fly ash obtained from a pilot-scale beneficiation run was used for this research. Three mixture ratios of alumina powder and fly ash were evaluated. The mixtures were mixed with water, ground in a ball mill, and then dried. The resulting powder blends were then die pressed into test coupons and reaction sintered. Appropriate sintering conditions were determined empirically by processing initial coupons using several different temperature-time combinations and then evaluating these coupons using a combination of X-ray diffraction and relative density measurements. For comparison, as-received, unbeneficiated fly ash was also processed into mullite using the same processing protocols.

The mullite samples fabricated from both the clean ash and the unbeneficiated ash were then evaluated to assess their water absorption (ASTM C373), density, Pyrometric Cone Equivalent (PCE) refractoriness (ASTM C24), Vickers hardness (ASTM E384), thermal expansion coefficient (ASTM E831), indentation fracture toughness, compression strength (ASTM C377), and sintering shrinkage. Similar tests were also performed on a commercial mullite for comparison. X-ray diffraction analyses on the samples sintered at various temperatures and times revealed only mullite and corundum phases. No other detectable impurity phases were observed in any of the samples. The only difference between samples was their observed mullite/corundum ratio. Complete mullite formation was obtained by sintering above 1600°C.

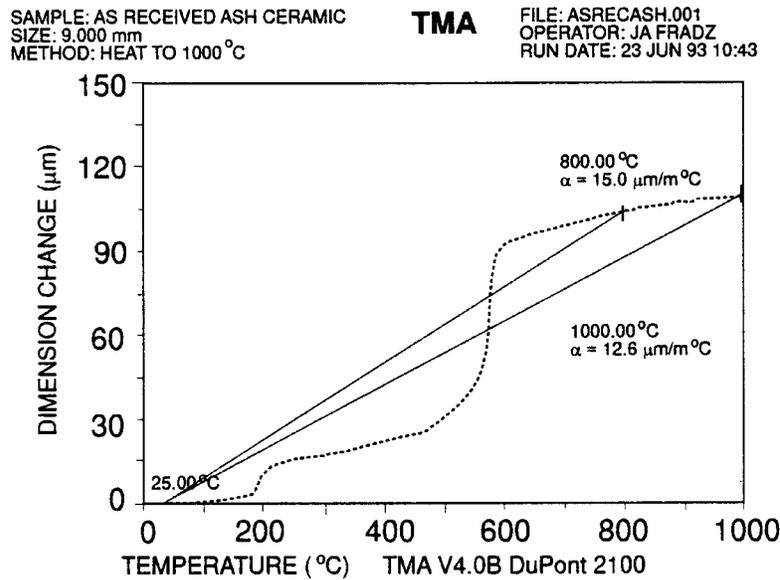
Table 6 summarizes the properties obtained on the mullites derived both the from clean and unbeneficated ashes. For comparison, properties of the commercial mullite are also included. Note that the mullite produced from clean ash exhibited water absorption, density, refractoriness, thermal expansion coefficient and fracture toughness values comparable to those of the commercial mullite. A slight difference in color between the two materials was observed, but this difference was not judged to be objectionable.

Table 6. Mullite Property Comparison									
Mullite Products	Water Absorp. Ratio, %	Density, g/cm <sup>3</sup>	PCE Cone, #	Vicker's Hardness kg/mm <sup>2</sup>	Thermal Expansion Coeff., 10 <sup>-6</sup> /°C	Fracture Toughness, MPa m <sup>1/2</sup>	Compressive Strength, MPa	Color	Sintering Shrinkage, %
Mullite FA-C82 (Clean Ash)	None	2.89	38	780	5.27	2.31	-	Yellow	15.4
Mullite FA-5-C115 (Clean Ash)	None	2.71	36	643	5.23	1.89	972	Yellow	11.2
Mullite FA5-A91 (As-received Ash)	0.21	2.80	38	722	9.28	2.51	988	Yellow	11.7
Commercial	None	2.82	38	-	4.5-5.3	2	-	Buff	N/A

Mullite derived from as-received fly ash (FA5-A91) exhibited a slightly higher water absorption ratio than materials made from clean ash. More importantly, however, the thermal expansion coefficient of this material was found to be 75% higher than the upper limit of the commercial mullite. Figures 7 and 8 show typical thermal expansion curves for mullites produced from both clean ash (FA5-C82) and unbeneficated ash (FA5-A91). The curve of the clean ash mullite shows uniform expansion with increasing temperature, but the curve for the as-received ash mullite shows a sudden expansion at about 570°C. The overall expansion coefficient of the as-received ash mullite from room temperature to 1000°C is much higher than that of the clean ash mullite.



**Figure 7. Typical thermal expansion coefficient curve of clean ash mullite.**



**Figure 8. Typical thermal expansion coefficient curve of as-received ash mullite.**

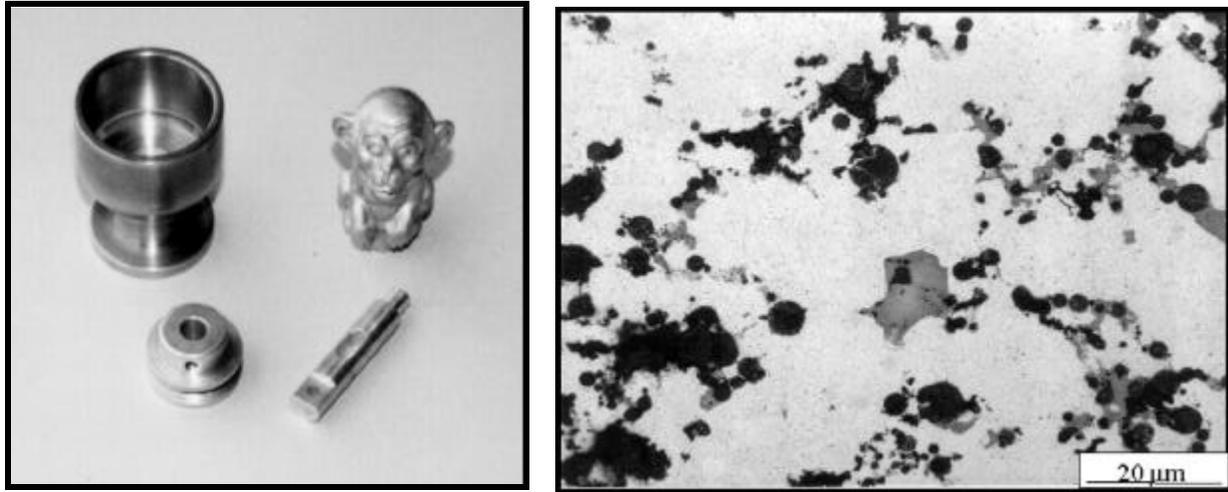
#### D. Metal Matrix Composites

Aluminum metal matrix composites represent an attractive, high-value-added, future market for processed fly ash. Over the last decade, discontinuously reinforced aluminum metal matrix composites have emerged as potential engineering materials for applications in a number of markets, including automotive, aerospace, electronic packaging and recreational products. These composites consist of a metallic aluminum matrix reinforced with blended-in hard ceramic particles. These ceramic particles typically increase both the strength and modulus of the aluminum alloy, as well as lower its coefficient of thermal expansion. They also produce a substantial increase in the wear resistance of the alloy. Examples of current discontinuously reinforced aluminum composites include Chevrolet Corvette and GM S/T pick-up truck drive shafts, Plymouth Prowler brake rotors and GM EV-1 brake drums, Toyota diesel engine pistons, guide vanes in Pratt & Whitney 4000 series jet engines, electronic packaging applications in both Motorola Iridium satellites and GM EV-1 vehicles, as well as bicycle components and golf clubs from several producers. [11]

These aluminum composites exhibit very attractive engineering properties, but they currently cost substantially more than alternative engineering materials. Accordingly, there is a well-recognized need to reduce the cost of these aluminum composites. Many of the current composites are produced using relatively expensive alumina or silicon carbide reinforcements. Work is now underway to assess the potential for using cleaned, sized fly ash as a low-cost alternative for these higher-cost ceramic additives.

Figure 9 illustrates some of the aluminum/fly ash composites which have been made to date. All were produced using conventional, powder-based aluminum composite processing. Metallic aluminum powder was first blended with 4.4 wt% copper powder and 1.5 wt% magnesium powder. This

blended elemental matrix alloy was then mechanically mixed with beneficiated, sized fly ash. Both beneficiation and sizing are essential for production of high-quality composites. The carbon and cenospheres in raw ash would degrade the mechanical properties of the composites, and the large particles present in un-sized ash would not mix homogeneously with the blended alloy matrix powders. The mechanically mixed composite powders were cold isostatically pressed into appropriate preforms. These preforms were then vacuum sintered or hot isostatically pressed (HIP'ped) to final density.



**Figure 9. Aluminum-Fly Ash Metal Matrix Composite formed products and micro-structure.**

Composite test pieces were fabricated containing both 10 vol% and 20 vol% fly ash. Materials containing higher ash contents tend to crack after cold pressing. Final densities of the 20 vol% material ranged from 88% of theoretical for the vacuum sintered material to 97.3% for the HIP'ped composites. The microstructure of the HIP'ped material is also shown in Figure 9. Note the relatively uniform dispersion of the spherical fly ash particles. Tensile tests on HIP'ped 20 vol% ash material which had been heat treated to a T-6 (peak strength) condition exhibited a tensile strength of 46,500 psi with 0.7% elongation. These properties are comparable to standard commercial pressed and sintered aluminum materials such as Alcoa 201AB-T6. Wear test data on the aluminum/fly ash composites are not yet available; it is anticipated, however, that these composites will exhibit substantially higher wear resistance than unreinforced aluminum materials such as 201AB-T6.

### **E. Carbon Adsorbents**

Activated carbon has been widely utilized in industry as an effective adsorbent. The Clean Air Act Amendments of 1990 identified mercury as an air toxic pollutant. The Environmental Protection Agency is required to establish emission control standards for mercury and its compounds from utility boilers. A portion of this study was therefore focused on evaluating the potential of using unburned carbon separated from fly ash for mercury adsorption.

Several carbons separated from fly ashes generated by American Electric Power (AEP), Detroit Edison (DE), and Nevada Power (NPC) have been studied. Properties of the carbon separated from each of the three ashes are shown in Table 7. Adsorption results obtained using the AEP carbon are reported here. This AEP carbon had an LOI (carbon content) of 80.90% and a BET surface area of 25.60 m<sup>2</sup>/g. For comparison, a commercial gas phase adsorption activated carbon from Calgon, (designated as BPL carbon) exhibited a BET surface area at 950 m<sup>2</sup>/g. An SEM image of the AEP carbon is shown in Figure 9. Adsorption tests were conducted using both batch and continuous methods. The batch tests were performed in a Tedlar bag to determine the adsorption isotherms. The continuous tests were performed in a column, primarily for the determination of adsorption kinetics. Both the AEP and commercial carbons were ground to -200 mesh before testing. The mercury concentration in the nitrogen carrying gas was determined with a Jerome 431-X gold film vapor analyzer.

**Table 7. Surface Area and Pore Size of AEP, DE, and NPC Carbons  
(Obtained by Nitrogen Adsorption Method)**

Carbons	AEP	DE	NPC
LOI	80.90	73.40	70.10
BET surface area, m <sup>2</sup> /g	25.60	18.71	58.33
Pore surface area (17-3000 Å), m <sup>2</sup> /g	20.26	12.83	38.43
Micropore area, m <sup>2</sup> /g	3.87	4.78	16.94
Pore volume (17-3000 Å), ml/g	0.0325	0.027	0.0586
Micropore volume, ml/g	0.0015	0.0021	0.0074
Average pore diameter (by BET),	49.97	48.87	43.74
Average pore diameter (by sorption),	64.23	71.15	61.01

Equilibrium adsorption isotherms of the two carbons at 20°C for various mercury concentrations are illustrated in Figure 10. At low gas phase mercury concentrations (<0.3 mg/m<sup>3</sup>), the mercury concentration in the carbon increases linearly and gradually with the increase in gas phase mercury concentration. When the gas phase mercury concentration exceeds 0.3 mg/m<sup>3</sup>, however, the mercury concentration in the carbon increases rapidly with increases in mercury concentration of the gas phase. Note that the AEP carbon has higher adsorption capacity at low mercury concentrations (<0.3 mg/m<sup>3</sup>), while the BPL carbon has higher adsorption capacity at high mercury concentrations (>0.3 mg/m<sup>3</sup>). The adsorption capacity of the AEP carbon is about 50 µg/g at 5 µg/m<sup>3</sup> gas mercury concentration and 70 µg/g at 280 µg/m<sup>3</sup> gas mercury concentration. Under the same condition, the Calgon BPL activated carbon has a capacity of 10 µg/g and 50 µg/g, respectively. The AEP carbon has an adsorption capacity about 5 to 7 times that of the BPL carbon at low mercury concentrations. Since the mercury concentration in emission gas from coal-fired power plants is usually in the range

of 0.04 to 0.2 mg/m<sup>3</sup>, the unburned carbon from fly ash may have an advantage over commercial carbon adsorbants.

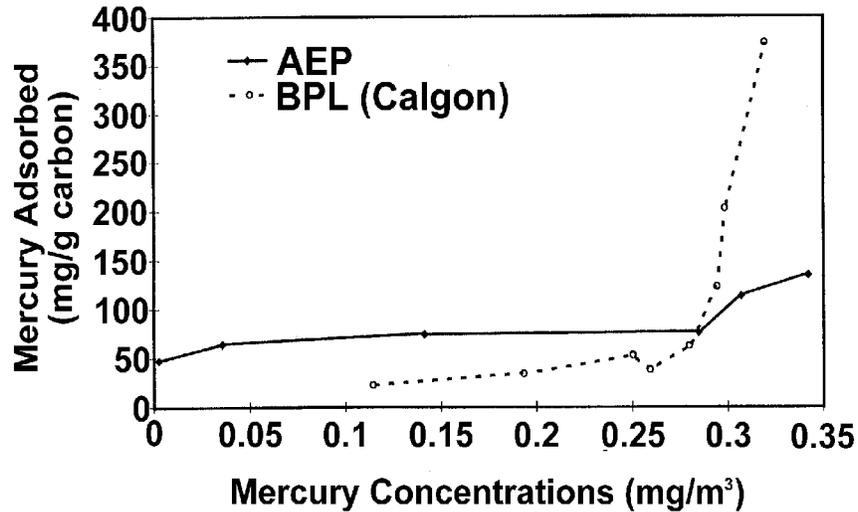


Figure 10. Isotherms of AEP carbon and Calgon BPL carbon for Hg vapor at 20 °C.

The adsorption capacity of the unburned carbons separated from fly ash can be further increased if this carbon is first heat treated in air before adsorption. Figure 11 shows the adsorption isotherms of two AEP carbons--one air-dried at 100°C and one air-dried at 400°C. The one dried at 400°C has a mercury adsorption capacity about 3 to 4 times that of the one dried at 100°C. If necessary, the fly ash adsorbants can also be regenerated after mercury exposure. Tests have been conducted to determine these regeneration requirements. By heating the carbon in air at 400°C for 4 hours, the mercury concentration in carbon can be reduced by 99.2%, as shown in Figure 12. If desired, the mercury evaporated from the carbon can be condensed for subsequent processing. As shown in Figure 13, regenerated carbon still retains its ability to adsorb mercury from flue gas,. The absorption capacity of this regenerated carbon, however, is approximately 30 to 40% lower than that of virgin carbon.

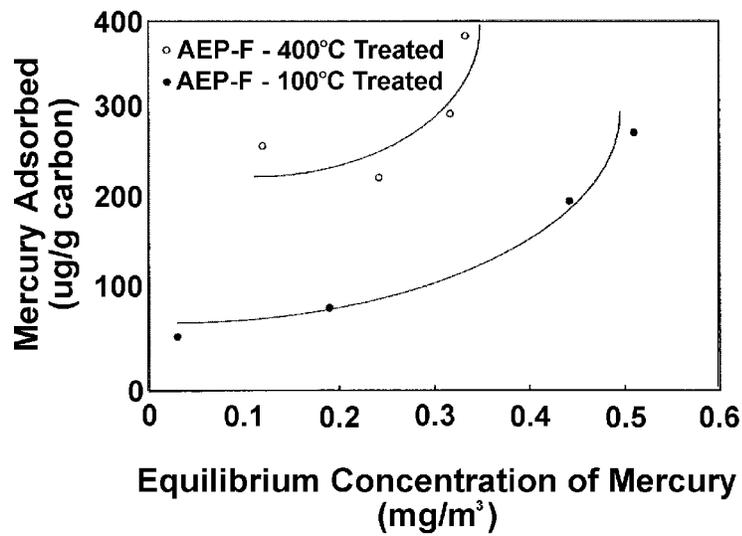


Figure 11. Adsorption Isotherms of AEP Carbons (from flotation process) at 20 °C.

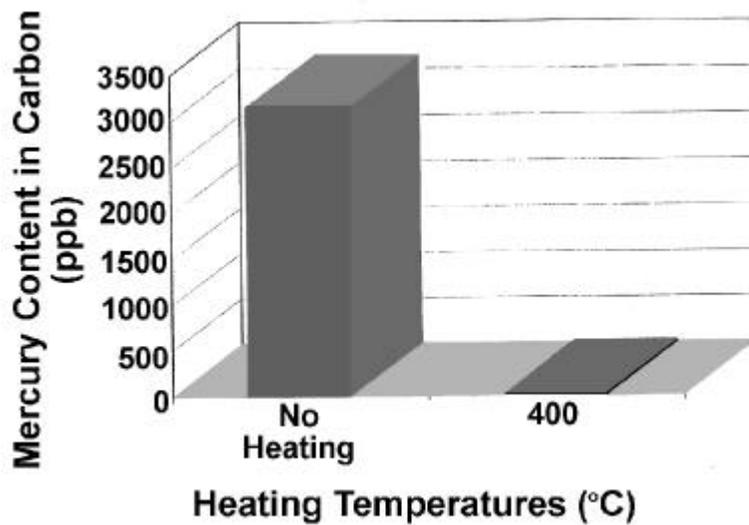
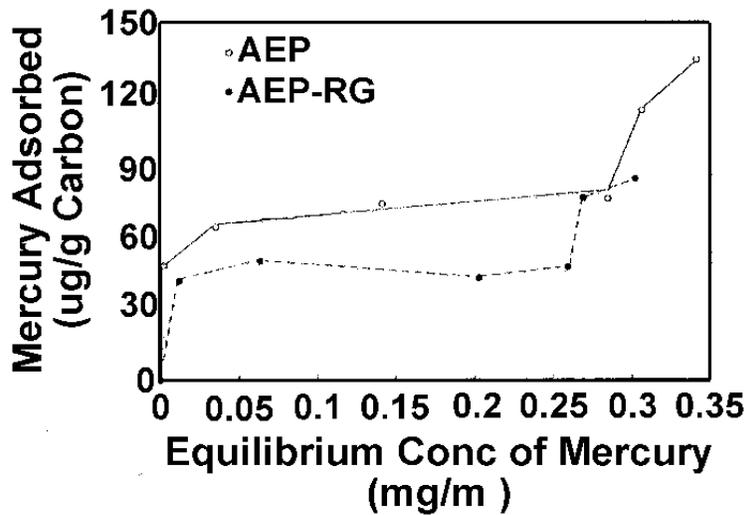


Figure 12. Effect of heating temperature on regeneration of AEP carbon (4 hours in air).



**Figure 13. Adsorption isotherms of AEP carbon and regenerated AEP carbon (AEP-RG) at 20 °C.**

### **Conclusions**

Low NO<sub>x</sub> combustion practices are critical for reducing NO<sub>x</sub> emissions from power plants. These low NO<sub>x</sub> combustion practices, however, generate high residual carbon contents in the fly ash produced. These high carbon contents threaten utilization of this combustion by-product.

This research has successfully developed a separation technology to render fly ash into useful, quality-controlled materials. This technology offers great flexibility and has been shown to be applicable to all of the fly ashes tested (more than 10).

The separated materials can be utilized in traditional fly ash applications, such as cement and concrete, as well as in nontraditional applications such as plastic fillers, metal matrix composites, refractories, and carbon adsorbents. Technologies to use beneficiated fly ash in these applications are being successfully developed.

In the future, we will continue to refine these separation and utilization technologies to expand the utilization of fly ash. The disposal of more than 31 million tons of fly ash per year is an important environmental issue. With continued development, it will be possible to increase economical, energy and environmental benefits by re-directing more this fly ash into useful materials.

### **Acknowledgment**

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